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An efficient and facile one-pot synthesis of structurally unique 2,4,6-tris(arylchalcogeno)-1,3,5-triazine and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene

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Dedicated to Professor Ram Charan Mehrotra (UOR) on his 82nd birthday

Abstract—An efficient one-pot synthesis of a novel class of 2,4,6-tris(arylchalcogeno)-1,3,5-triazine (sulfur, selenium and tellurium) and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene (sulfur and selenium)-containing ligands has been developed based on the reaction of 2,4,6-trichloro-1,3,5-triazine and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene with the corresponding arylchalcogenide anions generated in aqueous tetrahydrofuran.

There has been significant interest in the design and synthesis of robust organic ligands based on triazine and trimethylbenzene anchors due to their unique applications in organic synthesis,[1,2] enantiodifferentiating coupling reagents,[3] catalysis,[4] molecular tectonics,[5] polymeric materials[6] and in analytical[7] and coordination chemistry.[8] We also became interested in developing synthetic methodology for multifunctional organochalcogen (S, Se and Te) donors in order to create non-hydrogen-bonded networks, whereby chalcogen atoms could play an important role in the design and synthesis of highly diverse spatially arranged single components that may exhibit self-organizing properties through chalcogen–chalcogen interactions. In fact, the directional forces between chalcogen centres may lead to interesting structures when the chalcogen atoms are incorporated into fairly rigid ring systems. For these reasons, we paid attention to the synthesis of 2,4,6-tris(arylchalcogeno)-1,3,5-triazines and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzene.

Sodium areneselenolate and tellurolate ions, generated in situ by the reduction of the diaryldiselenide or diarylditelluride in aqueous THF with sodium borohydride at 0 °C, react with 2,4,6-trichloro-1,3,5-triazine and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene cleanly and afforded the desired 2,4,6-tris(arylchalcogeno)-1,3,5-triazines (selenium and tellurium) and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzenes, respectively, in excellent yields (>90%)[9] (Scheme 1). There is only a single report in the literature regarding the synthesis of $(PhE)_3C_3N_3$ (E = Se or Te) but the method cited therein is time consuming and tedious.[10] Moreover, the structural details of the compounds prepared were not discussed. The present method provides an efficient route for the synthesis of the desired compounds and suitable crystals of X-ray quality were obtained from diethyl ether solutions. Compounds **1**–**8** are crystalline in nature and soluble in common organic solvents when freshly prepared but showed decreased solubility after crystallization. Physicochemical and spectral studies were in good agreement with the proposed stoichiometry. ^{1}H and ^{13}C NMR spectral data showed no unusual features, suggesting in all cases, the equivalence of the RE^- groups as well as the ring carbons.

Single crystal X-ray diffraction studies of the compound $(PhTe)_3C_3N_3$ **2** revealed that the molecule crystallizes in

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Keywords: Arylchalcogen; Triazine; Sulfur; Selenium; Tellurium.

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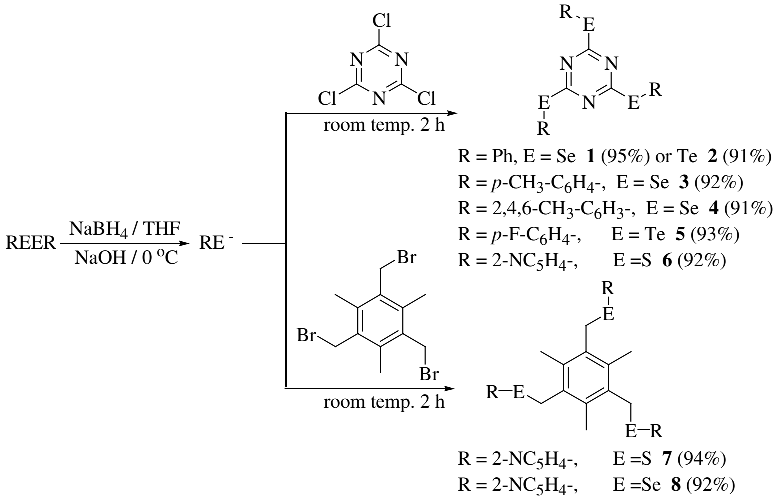

Scheme 1.

a monoclinic, $P2_1/n$, space group with four molecules per unit cell (Fig. 1). The triazine ring is essentially planar as the C–N bonds are consistent with a delocalized system[11] [1.325(8)–1.338(8) Å]. However, the triazine is not a regular hexagon, as the N–C–N bond angles and the C–N–C bond angles differ and a distortion similar to that found in s-triazine itself was observed.[12]

In compound **2** we encountered Te···Te distances of the order of 3.937 Å which is less than the van der Waals distance[13] (Te···Te = 4.40 Å). The distances between Te(1)–Te(2), Te(2)–Te(3) and Te(3)–Te(1) are 5.778, 5.810 and 6.033 Å, respectively, which further indicate that the triazine ring is distorted and forces the orientations of the two phenyltelluro rings towards each other. The substituted telluriums at the 2,4,6-positions are in close proximity with the nitrogens of the 1,3,5-triazine ring. Nevertheless, the atomic distances are worth mentioning (Te(1)···N(1), Te(2)···N(2) and Te(3)···N(3) are 3.015, 2.942 and 2.871 Å, respectively) and are larger than the sum of their covalent radii but significantly shorter than the sum of the corresponding van der Waals radii (3.61 Å).[14]

In summary, we have demonstrated a new and facile method for the reduction of diaryldiselenide or ditelluride with sodium borohydride in aqueous tetrahydrofuran for the generation of arylselenolate or tellurolate anions. Regrettably, the reduction of R_2Se_2 or R_2Te_2 has never received great attention in organic chalcogen chemistry due to its poor reactivity. However, addition of a few drops of water in tetrahydrofuran (aqueous THF) makes the reaction quite facile and generates arylselenolate or tellurolate ions, within a few minutes, which are both stable and easy to handle. We have also demonstrated a general, versatile and high yielding method for the construction of an aryl-heteroatom bond by preparing novel classes of 2,4,6-tris(arylchalcogeno)-1,3,5-triazines and 1,3,5-tris(arylchalcogeno)-2,4,6-trimethylbenzenes (sulfur, selenium and tellurium based robust ligands). Compounds **1**–**8** are quite appealing building blocks for the synthesis of metal complexes

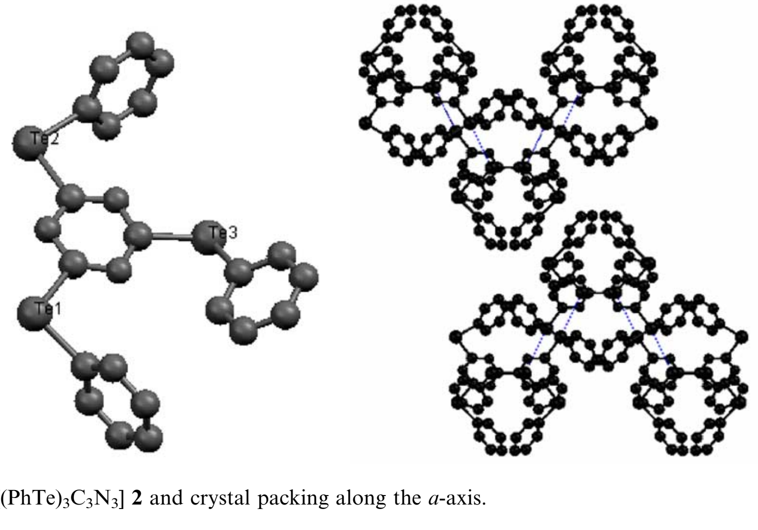

Figure 1. Crystal structure of $[(PhTe)_3C_3N_3]$ **2** and crystal packing along the *a*-axis.

where the S, Se and Te atoms may participate in bonding with metal ions. We are currently involved in examining their applications in creating *extended-reach structures* and results will be reported in due course.

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9. Typical procedure for the synthesis of **2**. To a stirred solution of diphenylditelluride (2.05 g, 5 mmol) and sodium hydroxide (0.040 g, 10 mmol) in aqueous THF (20 mL + 0.2 mL H_2O) under N_2 (g) and cooled to 0 °C was added $NaBH_4$ (0.419 g, 11 mmol) carefully. The orange-yellow colour of the ditelluride disappeared within a few minutes. The resulting mixture was allowed to warm to room temperature over 0.25 h. To the clear solution thus formed was added 2,4,6-trichloro-1,3,5-triazine (0.615 g, 3.33 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred for 2 h at room temperature and reaction completion was monitored by thin layer chromatography. The reaction mixture was concentrated to dryness and treated with saturated NH_4Cl solution (10 mL) and extracted with chloroform (3×20 mL). The combined organic extracts were washed with water (2×20 mL) and dried ($MgSO_4$), and concentrated to afford a colourless oil. This was washed with diethyl ether to yield the desired product of sufficient analytical purity. Diethyl ether washings also produced crystals of the desired species of X-ray quality on evaporation of the diethyl ether at room temperature. mp 98 °C. Elemental analysis for $C_{21}H_{15}N_3Te_3$ (%) calcd: C 36.44; H, 2.18; N, 6.07; found: C 36.32, H 2.03 and N 5.91. FAB-MS: *m*/*z* 699 for [M + H]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.01 (m, 9H, *m*- and *p*-Ph), 7.74–7.63 (m, 6H, *o*-Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.42, 139.23, 129.29, 128.76, 114.23.
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11. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.334(9), N(2)–C(2) 1.325(8), N(3)–C(2) 1.328(9), N(1)–C(3) 1.338(8), N(2)–C(1) 1.325(9), N(3)–C(3) 1.330(8), Te(1)–C(1) 2.112(6), Te(2)–C(2) 2.111(7), Te(3)–C(3) 2.100(7); C(1)–N(2)–C(2) 115.1(6), C(3)–N(1)–C(1) 112.8(6), C(3)–N(3)–C(2) 114.6(6), N(1)–C(3)–N(3) 126.4(6), N(1)–C(1)–N(2) 126.3(6), N(2)–C(2)–N(3) 124.8(7). Crystallographic data for compound **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 242546. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (+44-1223-336408; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
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